ON THE VARIATION OF COMPRESSIBILITY OF WATER AND ELECTROLYTIC SOLUTIONS WITH TEMPERATURE

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(*Received for publication, May 22, 1956; received after revision, February 7, 1958*)

ABSTRACT. Ultrasonic velocities and compressibilities in water and some electrolytes have been measured. The results have been discussed in the light of the knowledge about their structures.

INTRODUCTION

Variation of ultrasonic velocity in water with temperature upto near about the boiling point of water has been measured by Neuman (1947) and Willard (1947). They have employed the methods of interference and diffraction respectively for the determination of the velocity at the higher temperatures. The measurement of ultrasonic velocity at high temperatures tends to be inaccurate as the diffraction patterns become increasingly diffuse with temperatures near the boiling point. The velocities measured by these workers do not agree, particularly at higher temperatures and we have therefore attempted to measure the variation of velocity with temperature for water and also for solutions of NaCl and $MgSO_4$. The tabulated values of the densities from the International Critical Tables, Vol. III at different temperatures have been used to give us the respective compressibilities at different temperatures.

EXPERIMENTAL RESULTS

The velocities of ultrasonic waves in solutions were determined from the measurement of Debye Sears diffraction patterns, obtained by running a 50 watt ultrasonic generator at 3 m/c through the liquids. The liquids were heated to different temperatures upto about 90°C, by passing steam through a glass tube immersed in the trough containing the experimental liquids. The velocities at different temperatures and in different solutions were obtained by comparison with the fringe width dw for water at a lower range of temperature, where the velocity V_w is accurately known from measurements of other workers. The unknown velocity is determined from the relation $V_x\, dx = V_w\, dw$, where V_x and dx represent the velocity to be determined and the corresponding fringe seperation respectively. The ultrasonic frequency and the photographic set-up were kept

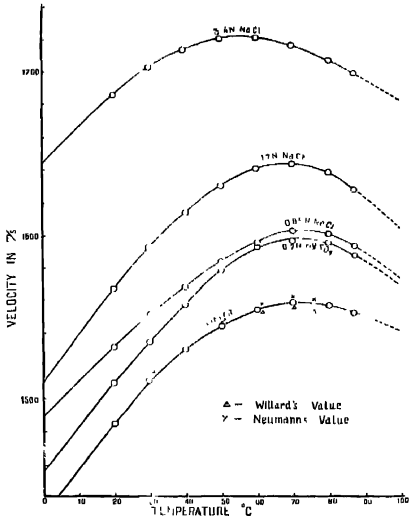
VELOCITY IN M
1700
1600
1500
3·4N NaCl
1·7N NaCl
Willard's Value
Neumann's Value
0
10
20
30
40
50
60
70
80
90
100
TEMPERATURE °C

Fig 1.

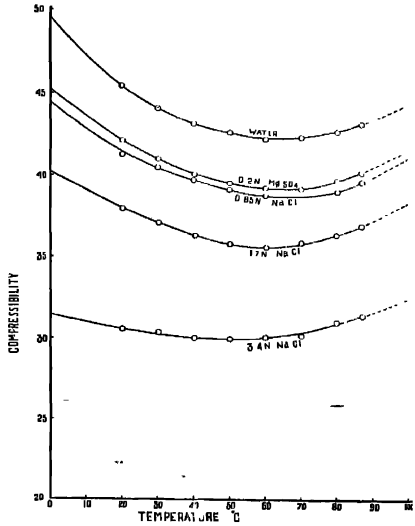
COMPRESSIBILITY
50
45
40
35
30
25
20
WATER
0·2N MgSO4
0·85N NaCl
1·7N NaCl
3·4N NaCl
0
10
20
30
40
50
60
70
80
90
100
TEMPERATURE °C

Fig 2.

constant throughout the experiment. The velocities so determined for the experimental liquids have been plotted in figure 1 against the temperatures with extrapolations below room temperature and above 90°C. The electrolytes and their molar strengths and also the experimental points of Neuman and Willard for water have been indicated on the figures. The probable error in the measurement of velocity is of the order of ± 1 m/s. The calculated values of compressibilities obtained from these velocity values and the known density values have been shown in figure 2.

DISCUSSIONS

It will be observed from the compressibility graphs in figure 2 that the compressibilities for water as also for the electrolytic solutions at first decreases and then rises with temperature. To account for these, qualitatively, we take up the composition of water as proposed by Bernal and Fowler (1933). We may consider that at about 0°C. water consists of the tridymite structures mostly, which break up partially into the cubical structures by the rise of temperature or by the influence of the ionic pull.

According to the accepted ideas, the cubical water structure, so formed, tends to be more closely packed due to larger mutual attraction upon one another. This naturally tends to decrease the compressibility by rise of temperature. Further, according to the theory of Bernal and Fowler the structure of water near about 100°C is of the homogeneous cubical type. The decrease of compressibility with the increasing strength of any electrolyte at this temperature, as will be observed from the graphs, cannot therefore be due to the breaking up of more complex structure It must be purely an effect of ionic pull on the polarised water structures which increases proportionately with electrolytic strength. This effect is, however, expected to be weaker for larger mutual separations caused by any rise of temperature and thus causing an increased compressibility with temperature.

Besides, as in the case of all non-associated pure liquids, there should occur an increase of compressibility on account of larger mutual seperations, if there is any, as the temperature rises. The variation of compressibility for electrolytes with the rise of temperature is thus caused by the following effects, namely, the general increase of compressibility with larger spacings as for any homogeneous non-associated liquids; the increase of compressibility due to diminished strength of ionic pull at larger seperation, by the effect of temperature rise, and the increased ionic attraction, and a further decrease of compressibility due to the effect of the broken up cubical structure. It does not appear to be feasible at this stage to sort out the magnitude of the different effects. The comparative value of the decrease of compressibility for different concentrations of NaCl

and $MgSO_4$ indicates that the decrease of compressibility compared with water is proportional to the concentration and the bivalent salts give rise to an effect which appears to be nearly double the ionic charge or the square of the charge. Further experiments on this line are expected to give fruitful results.

ACKNOWLEDGMENTS

Our thanks are due to Prof. A. K. Dutta for his kind help and guidance throughout the course of the work.

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Neuman, E. A., 1947, *Proc. Phys. Soc. Lond.*, **59**, 585.
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